

Boosting the electronic and catalytic properties of 2D semiconductors with supramolecular 2D hydrogen-bonded superlattices

Can Wang

Rafael Furlan de Oliveira, Kaiyue Jiang, Yuda Zhao, Nicholas Turetta, Chun Ma, Bin Han, Haiming Zhang, Diana Tranca, Xiaodong Zhuang, Lifeng Chi, Artur Ciesielski^{1,*} & Paolo Samorì^{1,*}
Université de Strasbourg, CNRS, ISIS, 8 allée Gaspard Monge, 67000 Strasbourg, France.
can.wang@unistra.fr, samori@unistra.fr

Abstract

The van der Waals heterostructures (vdWHs) formed by arbitrary stacking dangling-bond-free 2D nanosheets enabled the further diversification of the properties as a result of the charge redistribution at the interfaces of different 2DMs' crystals. Artificial vdWHs can be produced by using diverse strategies, such as the pick-and-lift technique and wet-transfer from chemical vapor deposition (CVD) samples. However, all these methods suffer from the lack of control over the lattice alignment at the interface between two 2D nanosheets. Moreover, the transferred layers can exhibit microcracks, wrinkles, and contaminations by residues from the often-employed sacrificial layers. In this context, the use of the supramolecular networks represents a simple, yet remarkably effective solution to overcome the problems. 2DMs provide atomically flat surfaces for molecular assembly governed by non-covalent interactions. The physisorption of suitably designed molecules allows the formation of self-assembled monolayers (SAMs) under thermodynamic control which represent true superlattices on top of the crystalline 2DMs. The presence of electron-donating/withdrawing groups in the molecule employed to form the SAMs can lead to doping of 2DMs through the controlled local modifications of their surface potential. Compared to molecules randomly adsorbed on the 2DMs, the use of highly ordered superlattices may maximize the electronics variation via collective or even cooperative effects.

Here, we study the effect of the physisorbed CA·M bi-component self-assembled network on the electronic properties of the underlying TMDCs. We found the occurrence of a strong charge transfer process taking place on TMDCs as characterized by a positive cooperative effect emerging in densely packed CA·M bi-component tri-hapto hydrogen bonded networks. Hybrid van der Waals heterostructures based on molybdenum disulfide (MoS₂) functionalized with CA·M supramolecular lattices exhibit an increase in charge carrier density, exceeding 10¹³ cm⁻². Moreover, the same superlattice grown on tungsten diselenide (WSe₂) also displays similar significant improvement of the electronic transport through the 2D material. Further insights into the electronic effect of this functionalization approach are gained with density functional theory (DFT) calculations and Kelvin Probe Force Microscopy (KPFM). The efficient charge transfer from the physisorbed CA·M superlattice to the 2DMs determines an upward shift of the Fermi level (E_F) of the 2DM. The studies on MoS₂ as an earth-abundant and inexpensive material are essential for the implementation of clean energy technologies using hydrogen. The formation of MoS₂ based 2D heterostructures, e.g., graphene / MoS₂ and WS₂ / MoS₂, induces a built-in electric field formed among the dissimilar layers, enhancing the MoS₂ catalytic performance. The highly crystalline nature of the 2D CA·M network and its significant n-doping effect on the 2DMs induces a strong enhancement of the hydrogen evolution reaction (HER) activity of MoS₂, surpassing the performance of the standard polycrystalline platinum catalyst. The effect the CA·M superlattice shifts the HER overpotential of MoS₂ over 100 mV, yielding a small Tafel slope of 40 mV/dec.

References

- [1] Wang, C., Furlan de Oliveira, R., Jiang, K. et al. Boosting the electronic and catalytic properties of 2D semiconductors with supramolecular 2D hydrogen-bonded superlattices. Nat Commun 13, 510 (2022). <https://doi.org/10.1038/s41467-022-28116-y>

Figures

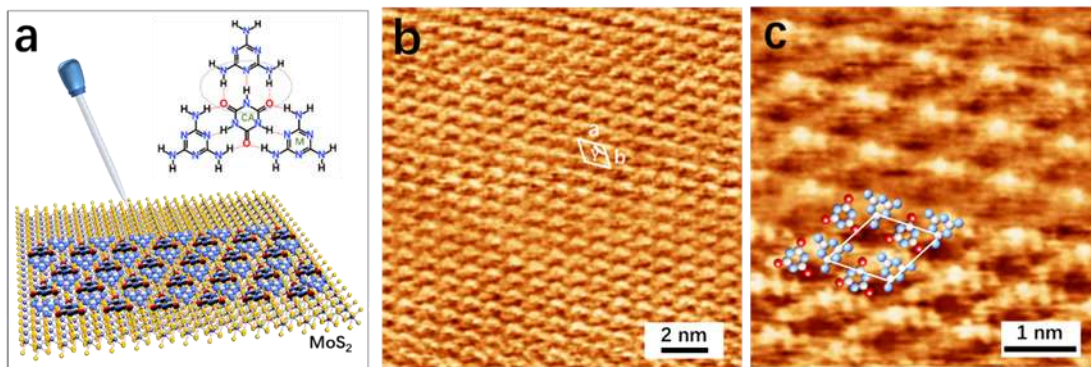


Figure 1: Supramolecular network of co-assembled CA·M monolayer onto monolayer MoS₂. (a) Schematic representation of the network formation, and the molecular structure of CA·M formed through hydrogen bonding between on monolayer MoS₂. (b, c) Scanning tunneling microscope height image of co-assembled network adsorbed onto MoS₂ surface, and its unit cell is denoted by a white rhombus. Unit cell parameters, i.e., vectors $a = b = 0.96 \pm 0.02$ nm, and the angle between them $\gamma = 120 \pm 2^\circ$ (b) survey (c) zoom-in with proposed molecular packing motif of CA·M.

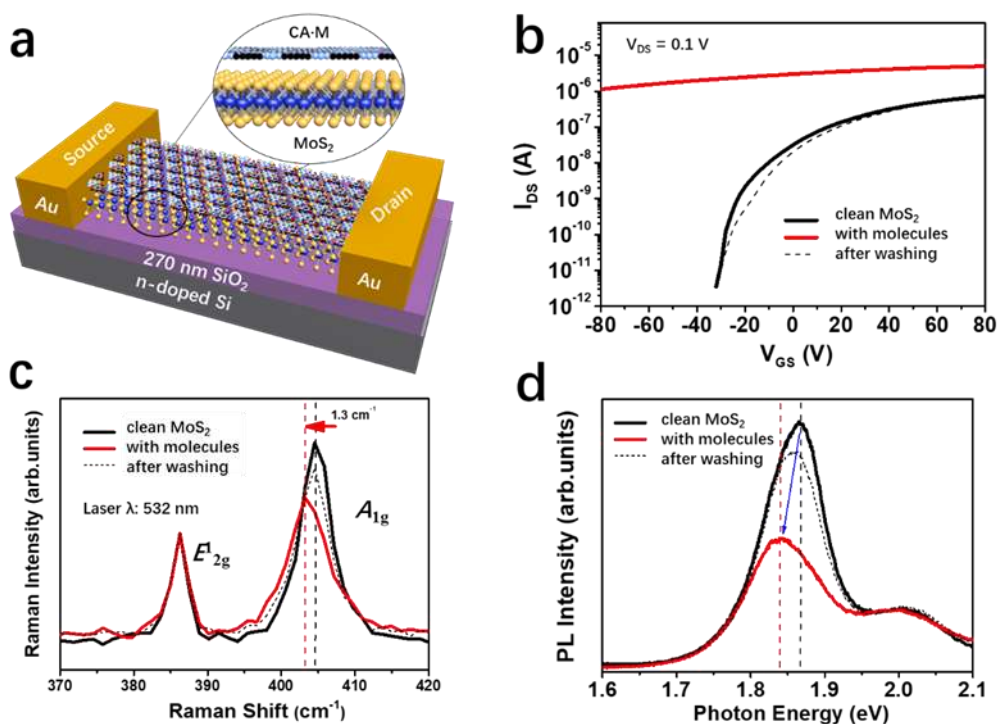


Figure 2: Electrical and spectroscopic characteristics of monolayer MoS₂ FET with and without the functionalization of melamine and cyanuric acid co-assembled supramolecular network (CA·M). (a) Schematics of the MoS₂ / CA·M hybrid device. (b) Transfer characteristics of MoS₂ FET. I_{DS} is the drain current and V_{GS} is the gate potential. (c) Raman and (d) Photoluminescence (PL) spectra of the device before (black curve) and after (red curve) CA·M functionalization, acquired under ambient conditions. As prepared MoS₂ samples (black solid), MoS₂ / CA·M (red solid), device after wiping the CA·M network (black dotted). The peak position is labeled with vertical dashed lines, MoS₂ in black and MoS₂ / CA·M in red. The arrows give the direction of the spectra shift: Raman A_{1g} peak shift in red and PL A exciton peak shift in blue.

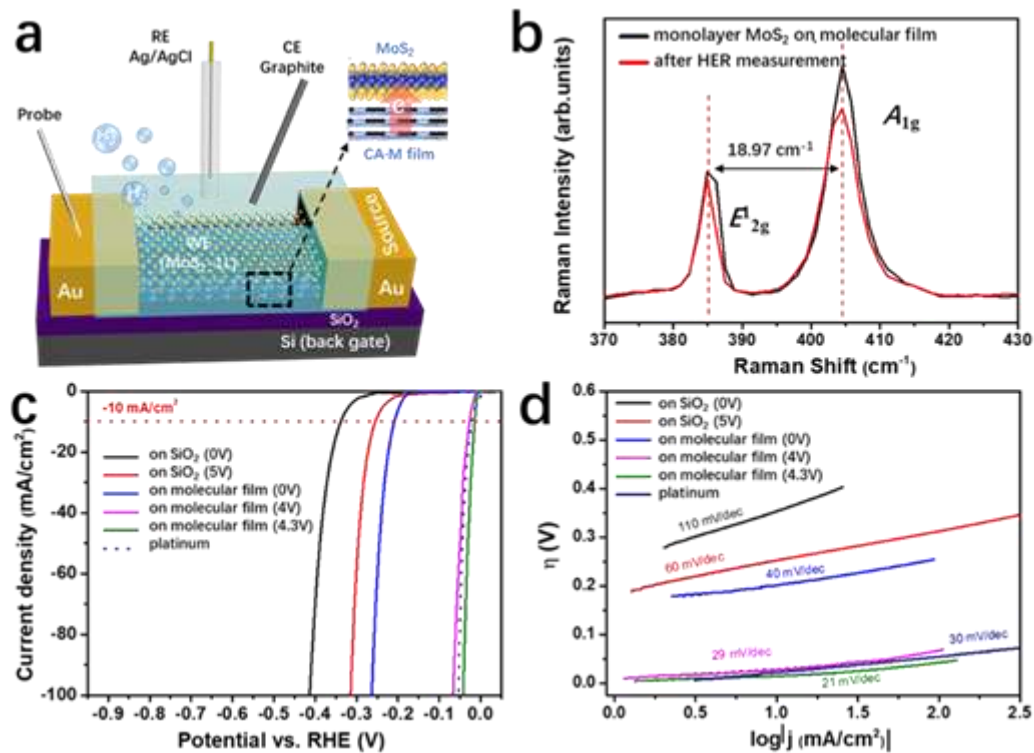


Figure 3: Hydrogen evolution reaction (HER) in the co-assembled supermolecule network (CA·M) / MoS₂ heterostructure. (a) Monolayer MoS₂ on CA·M molecular film device for HER measurements. The red arrow indicates the charge transfer direction in the heterostructure. (b) Raman spectra of the monolayer MoS₂ flake on CA·M before (black) and after (red) HER measurements, and Raman peak positions are marked by the dashed lines. (c) The polarization curves for HER on Platinum (dashed blue line) and monolayer MoS₂ flakes under different conditions (SiO₂ substrate with / without 2D CA·M buffer layer, and the respective voltages applied gate). The - 10 mA cm⁻² current density position is marked by the dashed red line. (d) Corresponding Tafel curves.